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MATERIALS AND METHODS FOR THE PRODUCTION AND PURIFICATION
OF
CHLOROFLUOROCARBONS AND HYDROFLUOROCARBONS

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FIELD OF INVENTION

The present invention is directed to production methods, as well as, synthetic and separation methods. More particularly, the present invention is directed to methods for manufacturing selective isomers of chlorofluorocarbons and hydrofluorocarbons from aliphatic, olefinic or partially halogenated hydrocarbons.

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BACKGROUND OF THE INVENTION

Since the beginning of global warming concerns, chlorofluorocarbon manufacturers have had to produce compounds that perform substantially the same as fully halogenated chlorofluorocarbons without the adverse environmental impact. Only through the introduction of these new compounds have their environmental impact been completely understood. In certain instances, some of these new compounds have been removed from the marketplace. These types of issues make the flooding agent, extinguishant, propellant and refrigerant production industry a dynamic and ever-changing marketplace where processes for the production of chlorofluorocarbons and fluorocarbons are advancing quickly to accommodate both environmental as well as economical requirements.

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Some useful compounds in this area include both saturated and unsaturated fluorocarbons, such as 1,1,1,2,3,3,3-heptafluoropropane ($\text{CF}_3\text{-CFH-}\text{CF}_3$, HFC-227ea), 1,1,1,2,2,3,3-heptafluoropropane ($\text{CF}_3\text{-CF}_2\text{-CHF}_2$, HFC-227ca) and hexafluoropropane (hexafluoropropylene, HFP, $\text{CF}_3\text{-CF=CF}_2$, FC-1216). One well known method of synthesizing these compounds begins with the chlorofluorination of propane, propylene or partially halogenated C-3 hydrocarbons with hydrogen fluoride (HF) and chlorine (Cl_2) in the presence of a metal-containing solid catalyst. Examples of this chlorofluorination step can be found in U.S. Patents 5,057,634 and 5,043,491 to Webster. As taught by Webster, the chlorofluorination step produces a number of saturated perhalogenated chlorofluorocarbons, including: (A) $\text{C}_3\text{Cl}_3\text{F}_3$; (B) $\text{C}_3\text{Cl}_4\text{F}_4$; (C) $\text{C}_3\text{Cl}_3\text{F}_5$; (D) 1,2-dichlorohexafluoropropane ($\text{CF}_3\text{-CClF-CClF}_2$, CFC-216ba); (E) 2,2-dichlorohexafluoropropane ($\text{CF}_3\text{-CCl}_2\text{-CF}_3$, CFC-216aa); (F) 1-

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Replacement sheet 1, Under Article 34

Empfangszeit: 6. Feb. 0:01

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Still another process for separating halogenation reaction products is provided wherein the reaction products are combined with water and cooled to a sufficient temperature to form a gas phase and top and bottom liquid phases. According to one embodiment, the gas phase contains primarily C-3 chlorofluorinated compounds having at least six fluorine atoms, the top liquid phase is primarily an aqueous liquid phase and the bottom liquid phase contains C-3 chlorofluorinated compounds having less than six fluorine atoms.

An additional process according to this invention provides for separating C-3 chlorofluorinated compounds from a halogenation reaction product. One embodiment of this invention includes the adjustment of a halogenation reaction product to a sufficient temperature to separate the reaction product into three phases: an upper gas phase and top and bottom liquid phases, wherein the upper gas phase contains primarily HCl, the top liquid phase contains HF and the bottom liquid phase contains essentially acid-free C-3 chlorofluorinated compounds.

In still another process of the present invention methods are provided for synthetically increasing the isomeric purity of a mixture. According to one embodiment, an isomeric mixture of C-3 chlorofluorinated compound isomers is heated in the presence of a catalyst to a sufficient temperature to increase the isomeric purity. In a more specific embodiment, the C-3 chlorofluorinated compound isomers are CFC-217ba and CFC-217ca.

In still another embodiment of the present invention a process is provided for selectively halogenating isomers within an isomeric mixture. In a particular embodiment, the isomeric mixture is exposed to Cl_2 in the presence of a catalyst at a sufficient temperature to halogenate at least one isomer. Preferably the isomeric mixture includes the isomers HFC-227ea and HFC-227ca.

The above and other embodiments, aspects, alternatives and advantages of the present invention will become more apparent from the following detailed description of the present invention taken in conjunction with the drawings.

Replacement sheet 5, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

DESCRIPTION OF THE FIGURES

Figure 1 is a schematic representation of one embodiment of the present invention.

Figure 2 is a graphical representation of the Isotherms observed during the processes of the present invention.

5 Figure 3 is a block diagram of an embodiment of the present invention.

Figure 4 is a block diagram of an embodiment of the present invention.

Figure 5 is a block diagram of an embodiment of the present invention.

Figure 6 is a block diagram of an embodiment of the present invention.

10 Figure 7 is a graphical representation of catalyst life observed according to an embodiment of the present invention.

Replacement sheet 6, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to Fig. 1, in one embodiment this invention provides processes for the production of chlorofluoropropanes and fluoropropanes from aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms. Other

5 embodiments of this invention provide specific processes for hydrodehalogenation, as well as, isomer and reaction product purification. Selected embodiments of this invention will be described in turn beginning with the broad chemical process steps used to produce selected chlorofluorocarbons and fluorocarbons.

10 In part, this invention stems from the discovery that the majority of the isomer in the final chlorofluorocarbon or hydrofluorocarbon product originates as an undesired isomer which forms in the initial reactions. This isomer and its downstream counterparts are passed to subsequent reactions undergoing the same chemical transformation as the desired isomeric material. Fortunately, CFC-216ba and its downstream counterparts, have different reaction profiles allowing for their reduction with each subsequent step. Unlike
15 CFC-217ca and HFC-227ca, CFC-216ba is not a "dead end" isomer. A majority of this material is directly converted to the desired isomer CFC-217ba in subsequent steps performed in accordance with the present invention.

Without being confined to any theory, the formation of the undesired isomer takes place in these early reactions by the premature fluorination of the geminal C-2 carbon of
20 aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms. The production of CFC-216ba is but just one example of this type of chemistry.

Referring now to Fig. 2, formation of excess amounts of CFC-216ba during halogenation has been observed when the reaction is allowed to exotherm excessively. The large amounts of energy released during this exotherm are probably the ultimate
25 reason for

Replacement sheet 7, Under Article 34

Empfangszeit 6. Feb. 2004

AMENDED SHEET

WO 03/029173

PCT/US02/30729

excess CFC-216ba isomer formation. When these types of conditions are allowed to prevail, ratios as low as 2:1 CFC-216aa:CFC-216ba can be observed in these early reaction streams.

One way to control this phenomenon can be to carefully operate the initial halogenations so as to avoid uncontrolled exotherms. The reactor used according to the present invention has the ability to use cool heat transfer oil and includes conventional chemical and engineering controls to insure suppression of exotherms. In another aspect of the present invention, HF can be replaced as the main diluent for the reaction. Figs. 3-4 show a schematic flow diagram for a process according to the present invention that includes a two temperature zone chlorofluorination of a C-3 reactant selected from propane, propylene, partially halogenated C-3 acyclic hydrocarbons, and mixtures thereof, with hydrogen fluoride and chlorine in the presence of a chlorofluorination catalyst. The process is highly selective in the production of CFC-216aa, without the formation of any significant amount of FC-218 (0 to less than 0.5 percent by weight). The high yield and selectivity of the process of the present invention in the synthesis of CFC-216aa is very advantageous for the subsequent production of HFC-227ea as discussed below.

The present invention provides, in one aspect, two step processes for efficiently producing CFC-216aa. The chemical steps can include the sequential replacement of hydrogen with chlorine and the subsequent partial replacement of chlorine with fluorine atoms. Multiple products may be formed with intermediate fluorinated materials being the majority. Careful temperature control may minimize by-product formation. Typical reaction products may include C-3 molecules with 2 to 7 fluorine atoms, the rest being chlorine. The cracking of the C-3 backbone to form C-1 and C-2 materials as undesired impurities has also been observed. According to one embodiment, the output of this reactor can be fed directly into a subsequent reactor as shown in Fig. 4, which is run at a higher temperature. Individual reactants may be fed under flow control to vaporizer(s) 14, as shown in Fig. 3. The vaporized chlorine and HF are mixed and fed into a superheater. It has been determined that careful mixing of the reactants and temperature regulation may help to control reaction exotherms and lack of control may lead to the formation of undesired by-products arising from cracking the C-3 backbone.

Replacement sheet 8, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

The predominant reaction occurring in exemplary chlorofluorination Steps I and II may be summarized, as follows, with high selectivity in the production of CFC-216aa:



(X=halogen; y=0-8, z=8-y; or y=0-6, z=6-y)

- 5 According to one aspect, the process includes a first step, wherein C-3 reactants selected from the group consisting of aliphatic, olefinic or partially halogenated hydrocarbons having at least three carbon atoms are contacted with Cl_2 and HF in the presence of a metal containing catalyst. As illustrated in Fig. 3, this reaction is preferably performed in the gas phase by the careful mixing of C-3 reactants with a mixture of
- 10 hydrogen fluoride (HF) and chlorine (Cl_2) in the presence of a metal containing catalyst at a sufficient temperature to form perhalogenated compounds.

- In one embodiment of the present invention, the C-3 reactant is selected from the group consisting of aliphatic, olefinic and/or partially halogenated hydrocarbons. The C-3 reactant may be premixed with hydrogen fluoride, and then mixed with chlorine before
- 15 entering chlorofluorination reactor 16 containing a fixed bed of metal containing catalyst.

- Aliphatic hydrocarbons having at least three carbon atoms are known to those skilled in the art to be alkanes, hydrocarbons characterized by a straight or branched carbon chain. These types of compounds include propane. Olefinic hydrocarbons having at least three carbon atoms are known to those having ordinary skill in the art to be
- 20 unsaturated aliphatic hydrocarbons having at least one double bond. These types of compounds include propene. Partially halogenated hydrocarbons having at least three carbon atoms are known to those having ordinary skill in the art as aliphatic or olefinic hydrocarbons wherein one or more hydrogens have been replaced by halogens.

- According to one embodiment of the present invention, the HF and C-3 reactants
- 25 are premixed before being combined with the chlorine gas and conveyed into a chlorofluorination reactor. It is preferred to premix (dilute) the C-3 reactant with the hydrogen fluoride reactant prior to combining the HF/C-3 gas reactants with the chlorine gas reactant in order to minimize the potential reaction of the C-3 reactant, e.g., propane and/or propylene with concentrated chlorine gas. Accordingly, at least one of the C-3
- 30 reactant or the chlorine, preferably both the C-3 reactant and chlorine, may be diluted with hydrogen fluoride prior to combining the C-3 reactant with the chlorine gas.

Replacement sheet 9, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

In one embodiment of the present invention the HF is anhydrous. It has been determined that recycled or reagent grade HF may be used. The type of HF used to perform this aspect of the invention is not critical and specific types and qualities will be recognized by those skilled in the art. The Cl₂ likewise is a matter of choice to those having skill in the art. In one embodiment, technical or pure-grade anhydrous Cl₂ is utilized.

The halogenation of aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms is a highly exothermic reaction which may be controlled through the use of excess quantities of hydrogen fluoride, a diluent, or an external heat transfer medium together or in combination, to absorb the heat evolved and to maintain temperature control of the mixture.

To reduce the impact of exotherms, preferably, a stoichiometric excess of hydrogen fluoride may be maintained in order to minimize decomposition of the C-3 reactant to C-1 and C-2 by-products, and the formation of the less desired CFC-216ba. Preferably, about 6 to about 64 moles of HF per mole of C-3 reactant may be utilized. It is preferred to provide an excess of chlorine gas as well, preferably about 8 to about 10 moles of Cl₂ per mole of C-3 reactant. However, an excess of Cl₂ is not required. In a preferred embodiment, the ratio of Cl₂ to C-3 reactants can be about 8.2:1. The molar ratio of HF to Cl₂ may be from about 0.75:1 to about 8:1. Preferably, the molar ratio of HF to Cl₂ may be about 4:1. Moreover, in another embodiment, a diluent may be added to the reaction to decrease undesired isomer and formation of cracking materials.

Preferably, the chlorofluorination reactor 16 used to perform this invention may be maintained at a reaction pressure of about 0 psig to about 750 psig, preferably about 0 psig to about 750 psig and at a temperature in the range of about 150°C to about 450°C, and preferably about 220°C. Residence time in chlorofluorination reactor 16 may be in the range of about 0.5 seconds to about 30 seconds and preferably about 5 to about 10 seconds. An exemplary reaction mixture exiting Step I shown in Fig. 3 is rich in C₃Cl₄F₄ and C₃Cl₃F₅, but may also contain CFC-216aa and many other under fluorinated compounds. In an exemplary aspect, reaction products of this first step are conveyed directly to Step II, as shown in Fig. 4. However, it is recognized that the reaction products of Step I, as shown in Fig. 3, may be further purified or supplemented prior to continuing on to Step II. A main goal in Step II can be the selective fluorination of under-fluorinated compounds to the desired isomer CFC-216aa.

Replacement sheet 10, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

In the illustrated embodiment, the second step in this process may replace all of the terminal chlorine substituents with fluorine to produce CFC-216aa. According to one aspect of the present invention, this is accomplished through the use of one or more of high temperature reaction conditions, excess HF, and a metal containing catalyst.

5 As shown in Fig. 4, the Step I reaction stream is directly fed into a superheater 24. Optimally, this stream is then fed to Step II reactor 26. Again, as before in Step I, careful temperature regulation can be used to control the reaction.

The second reaction can take place either in the same reactor as exemplary Step I or, preferably, in a second reactor. The second reaction can be carried out at a higher
10 temperature than the first reaction with a stoichiometric excess of hydrogen fluoride. According to one embodiment, a stoichiometric excess of chlorine can be used to ensure chlorofluorination of the first reaction products.

Reactor 26 can be a fixed-bed reactor having a metal containing catalyst, maintained at a reaction pressure of about 0 psig to about 750 psig and preferably about
15 100 psig, and at a temperature higher than the temperature required in exemplary Step I. Step II may occur at a temperature ranging from about 300°C to about 550°C, and preferably at about 470°C. It is preferred that the molar ratio of reactants in Step II, should be maintained at about 6 to about 64 moles of hydrogen fluoride per mole of perhalogenated compounds. As in Step I, the source and quality of anhydrous HF used in
20 Step II is not critical. It is to be understood by those skilled in the art that anhydrous, recycled, and/or differing grades of HF can be used in Step II. As in Step I, a diluent may be added to control exotherms and increase isomeric yield.

The metal containing catalyst used in Step I or Step II can be any known catalyst useful for reacting C-3 reactants or perhalogenated compounds with HF and/or Cl₂,
25 including those described in U.S. Patent Nos. 5,177,273 and 5,057,634 to Webster, hereby incorporated by reference. These catalysts include catalysts consisting essentially of chromium; catalysts consisting essentially of chromium oxide in combination with a support (e.g. refractory oxide); catalysts consisting essentially of chromium oxide modified with up to about 10 percent by weight based upon the weight of chromium in the catalyst
30 of metal selected from the group consisting of manganese, iron, cobalt, nickel, copper, zinc, other metals and mixtures thereof; and catalysts consisting essentially of chromium oxide in combination with the refractory oxide and modified with up to about 10 percent by weight based upon the

Replacement sheet 11, Under Article 34

Empfangszeit 5. Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

under reaction conditions is considered an equivalent procedure within the scope of this invention.

In this and the other reaction sequences, reaction with HF includes either high temperature vapor phase reaction or lower temperature reaction in the presence of a liquid phase catalyst such as SbCl_5/HF or SbF_5 ; the vapor phase process is preferred.

Two metal containing catalysts that have been found to be particularly useful for the chlorofluorination reactions include:

(1) FeCl_3 on a support, particularly active carbon, that is dried and then fluorinated, e.g., with HF, preferably an HF/N_2 mixture, with or without O_2 , at about 200°C to about 270°C and then treated with HF, with or without O_2 or Cl_2 activation, within the range of about 270°C to about 320°C . It is preferred that the percent by weight of FeCl_3 in the metal containing catalyst be in the range of about 2% to about 36% by weight on a catalyst support, which is preferably activated carbon, preferably at about 5% to about 10% by weight FeCl_3 . It is useful to fluorinate the metal containing catalyst for a period of at least about 2 hours, preferably about 2 to about 16 hours, more preferably about 8 hours, gradually increasing the temperature within the range of from about 200°C to at least the chlorofluorination reaction temperature, e.g., up to about 320°C ; and

(2) CrCl_3 , particularly chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) on a support, particularly active carbon, that is dried and then fluorinated, e.g., with hydrogen fluoride gas (HF), in the same manner as fluorination of the FeCl_3 catalyst with or without O_2 or Cl_2 activation.

Non-limiting examples 1, 2 and 3 demonstrate the preparation of catalysts suited for the present invention and non-limiting example 4 demonstrates the activation of catalyst suited for this invention.

Generally, all fluorination catalyst can be prepared by mixing appropriate amounts of the selected metal salt and support (if necessary) in DI Water. This mixture may be allowed to stand for approximately 0.5 hour and the excess water can be filtered off by vacuum filtration. The resulting solid may then be dried overnight in a gravity oven at 115°C and then charged to the reaction tubes where it can be further dried at 150°C with a inert gas purge and then activated with HF before the reaction feeds are started.

Replacement sheet 13, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

Table 6. Chlorofluorination Organic Phase Removed from HF According to a Process of the Present Invention

	Area % Cl ₂	Area % HF	Area % HCl	Area % Organic
Separated Organic Phase	1.21	0.3872	0.6097	97.79

Table 7. Halogenated Organics Separated from HF According to the Present Invention

Halogenated Organics	Percentage of Total Organics
CCl ₃ F-CClF ₃	not detected
Lights	0.05
C ₃ Cl ₂ F ₆	64.59
C ₂ Cl ₂ F ₃	11.82
C ₃ Cl ₄ F ₄	5.75
Heavies	3.65

As this example demonstrates the organic phase, once separated according to an embodiment of the present invention, is essentially acid-free. This allows for the immediate isolation of specific chlorofluorination reaction products without the need for costly and inefficient distillation. Moreover, Table 7 demonstrates that other halogenated organics can be separated from HF, according to the present invention. These chlorofluorination reaction products can be isolated according to another process of the present invention as herein described next.

Another process according to the present invention is the separation of the C-3 chlorofluorinated compounds having at least six fluorine atoms from C-3 chlorofluorinated compounds having less than six fluorine atoms. This separation process is extremely useful in order to maintain the compound purity of chlorofluorinated compounds sought to be produced.

According to one embodiment of the present process, a solution comprising C-3 chlorofluorinated compounds having at least six fluorine atoms and C-3 chlorofluorinated compounds having less than six fluorine atoms is provided. This solution is derived from a reaction product or a refined reaction product of a chlorofluorination reaction or the phase separation or distillation product after a chlorofluorinated reaction. In one embodiment of the present invention the C-3 chlorofluorinated compounds having at least six fluorine atoms comprises CFC-216aa. However, this invention is not limited to the source of this mixture.

Replacement sheet 26, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

chlorofluorinated compounds having at least six fluorine atoms are conveyed to an additional reaction step to increase the number of fluorine atoms present.

Example 10: Separation of Fluorinated Compounds:

The containers of crude $C_3Cl_2F_6$ from various production runs of Steps I and II contained $C_3Cl_2F_6$ and numerous other unidentified underfluorinated compounds, and possible small amounts of H_2O , HF , Cl_2 , and HCl .

Approximately 73 kg of crude $C_3Cl_2F_6$ were fed from a heated cylinder to a 57 liter Halar[®] lined scrubber tank. The scrubber tank contained a level gauge and an external heat tracing with a skin temperature thermocouple. The feed line into the tank was through a dip tube.

The tank was initially filled with a 5% KOH/water solution and the temperature of the tank was heated to 50°C. The mixture separated into three phases: an upper, primarily gaseous phase; a top liquid, primarily aqueous phase; and a bottom primarily organic phase. The top gas phase was removed as a vapor stream and fed to a Halar[®] lined scrubber. The vent gas was open to a molecular sieve dryer bed which fed into a chilled collection cylinder on a scale. Upon completion of the scrubbing of the $C_3Cl_2F_6$, the underfluorinated organics collected from the bottom phase was approximately 9.1 kg of material. The primary components of this organic liquid were $C_3Cl_2F_4$, and $C_3Cl_3F_5$ and $C_3Cl_2F_6$.

Table 8. Results of Separation of Underfluorinated Separation According to the Present Invention

Separated Phase	Constituents
Vapor	Essentially pure $C_3Cl_2F_6$
Bottom	-6% $C_3Cl_2F_6$ and -94% underfluorinated compounds

As table 8 demonstrates, underfluorinated compounds can be efficiently separated from $C_3Cl_2F_6$ according to the present invention.

As shown in Fig. 5, the present invention provides a third reaction step (Step III) for the selective fluorination of $C_3Cl_2F_6$ to CFC-217ba. The predominant reaction occurring in this step is as follows: $C_3Cl_2F_6 + HF \rightarrow CF_3-CFCl-CF_3 + HCl$

Preferably, Step III proceeds in the gas phase with excess anhydrous HF over a metal containing catalyst. According to one embodiment of the present invention,

Replacement sheet 28, Under Article 34

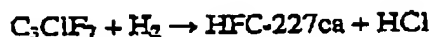
Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/028173

PCT/US02/30729

hydrodehalogenation reaction products include HFC-227ca. A reaction of this embodiment is shown below:



- A slight molar excess of H_2 can be used if desirable but is not necessary. The
- 5 H_2 :halogenated organic compound molar ratio is in the range of about 0.2:1 to about 10:1, optimally about 1.2:1.

- Referring now to Fig. 6, the hydrodehalogenation is performed in fixed bed reactor 42 containing a suitable catalyst, such as palladium on a refractory oxide support, such as alumina or other suitable supports, in which case the reactor is operated at a temperature of
- 10 about 30°C to about 275°C, and preferably at about 185°C. Alternatively, a ferric chloride (FeCl_3) catalyst on a solid support, such as active carbon can be used in which case the reactor is operated at a temperature of about 200°C to about 600°C, and preferably at about 450°C to about 500°C.

- The pressure in reactor 42 should be in the range of about 1.2 Pa to about 15 Pa,
- 15 and preferably about 7.9 Pa. The reaction is largely insensitive to pressure in the range of 0.9 – 7.9 Pa, however, reaction selectivity is slightly favored by lower pressures. Residence time in reactor 42 should be in the range of about 10 seconds to about 90 seconds, and preferably about 15 to about 60 seconds.

- While any hydrodehalogenation catalyst could be used, the most active catalysts,
- 20 such as Pt and Pd, are good selections because, in addition to the desired products, they lead to the addition of hydrogen across any double bond present or to the substitution of hydrogen for chlorine. Catalysts which may be utilized include, as charged to the reactor, common hydrogenation catalysts such as Cu, Ni, Cr, Ru, Rh or combinations thereof. It is not critical whether the catalysts are supported or not. However, supports which are
- 25 unreactive to halocarbons, HF, and oxygen at hydrogenation temperatures up to 100°C higher such as metal fluorides, carbon, and titanium, may be used.

- Referring now to Fig. 7, the high cost of noble metals led to concerns regarding catalyst lifetime. Initial testing demonstrated that the catalyst is somewhat fragile with activity dropping off within 5 days. Fortunately, it has been discovered that the addition of
- 30 a small amount of water to the reaction stream extended catalyst lifetime. The addition of water allows the catalyst to perform in excess of 15 days.

Replacement sheet 37, Under Article 34

Empfangszeit 6.Feb. 07:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

As Table 21 demonstrates, the present invention can be used to even further reduce the content of the undesired isomer. It is contemplated that once reduced the more isomerically pure reaction product can be recycled or further refined.

Replacement sheet 52, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

What is claimed is:

1. A process for producing $\text{CF}_3\text{CCl}_2\text{CF}_3$ comprising:
contacting a C-3 reactant comprising one or more of perhydrogenated or partially halogenated C-3 hydrocarbons with Cl_2 and HF in the presence of a first catalyst
5 at a first temperature to form a C-3 product comprising a C-3 perhalogenated compound, wherein the first catalyst comprises chromium and the first temperature is less than 450°C ; and
contacting the C-3 product with HF in the presence of a second catalyst at a second temperature different from the first temperature to form $\text{CF}_3\text{CCl}_2\text{CF}_3$, wherein the
10 second temperature is greater than 300°C .
2. The process of claim 1 further comprising contacting the $\text{CF}_3\text{CCl}_2\text{CF}_3$ with HF in the presence of a third catalyst to form $\text{CF}_3\text{CClF}_2\text{CF}_3$.
3. The process of claim 2 further comprising contacting the $\text{CF}_3\text{CClF}_2\text{CF}_3$ with H_2 in the presence of a fourth catalyst to produce $\text{CF}_3\text{CFHCF}_3$.
- 15 4. The process of claim 3 further comprising, during the contacting of the $\text{CF}_3\text{CClF}_2\text{CF}_3$ with H_2 , contacting the fourth catalyst with water.
5. The process of claims 1, 2, 3, or 4 wherein the first temperature is from 150°C to less than 450°C and the second temperature is less than 550°C .
6. The process of claims 1, 2, 3, or 4 wherein the first temperature is at least
20 220°C and the second temperature is at least 470°C .
7. The process of claims 1, 2, 3, or 4 wherein, during the contacting of the C-3 reactant with the HF and the Cl_2 , a molar ratio of the HF to the Cl_2 is from 0.75:1 to 8:1.
8. The process of claims 1, 2, 3, or 4 wherein, during the contacting of the C-3 reactant with the HF and the Cl_2 , a molar ratio of the HF to the Cl_2 is at least 4:1.
- 25 9. The process of claims 1, 2, 3, or 4 wherein, during the contacting of the C-3 reactant with the HF and the Cl_2 , a molar ratio of the Cl_2 to the C-3 reactant is from 8:1 to 10:1.
10. The process of claims 1, 2, 3, or 4 wherein the second catalyst comprises chromium and a catalyst support.
- 30 11. The process of claim 2, 3, or 4 wherein the contacting the $\text{CF}_3\text{CCl}_2\text{CF}_3$ with HF in the presence of a third catalyst occurs at a temperature of at least 200°C .

Replacement sheet 53, Under Article 34

Einfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

12. The process of claims 2, 3 or 4 wherein, during the contacting of the C-3 product with the HF, a molar ratio of the HF to the C-3 product is at least 30:1.
13. The process of claims 2, 3, or 4 where during the contacting of the $\text{CF}_3\text{CCl}_2\text{CF}_3$ with the HF, a molar ratio of the HF to the $\text{CF}_3\text{CCl}_2\text{CF}_3$ is at least 10:1.
- 5 14. The process of claims 2, 3, or 4 wherein the third catalyst comprises chromium and a catalyst support.
15. The process of claim 3 or 4 wherein the contacting the $\text{CF}_3\text{CClFCF}_3$ with H_2 in the presence of a fourth catalyst occurs at a temperature of at least 30°C .
- 10 16. The process of claims 3 or 4 wherein, during the contacting of the $\text{CF}_3\text{CClFCF}_3$ with the H_2 , a molar ratio of the H_2 to the $\text{CF}_3\text{CClFCF}_3$ is at least 1.2:1.
17. The process of claim 3 or 4 wherein the fourth catalyst comprises palladium and a catalyst support.
18. The process of claim 4 wherein the water is present in an amount from 0.04 to 12 percent by weight of the $\text{CF}_3\text{CClFCF}_3$.
- 15 19. The process of claim 20 wherein the amount is 0.8 percent by weight of the $\text{CF}_3\text{CClFCF}_3$.
20. A hydrogenation process comprising contacting a compound with a catalyst in the presence of water to form a hydrogenated compound.
21. The process of claim 22 wherein the contacting further comprises
- 20 contacting the compound with H_2 .
22. The process of claim 20 wherein a ratio of the H_2 to the compound is from 0.2:1 to 10:1.
23. The process of claims 22 or 23 wherein a ratio of the H_2 to the compound is at least about 1.2:1.
- 25 24. The process of claims 22 or 23 wherein the water is from about 0.04 to about 12 percent by weight of the compound.
25. The process of claims 22 or 23 wherein the water is at least about 0.8 percent by weight of the compound.
26. The process of claims 22 or 23 wherein the catalyst contains a metal.
- 30 27. The process of claims 22 or 23 wherein the catalyst comprises palladium and a catalyst support.
28. The process of claims 22 or 23 wherein the compound comprises $\text{C}_3\text{F}_7\text{Cl}$ and the hydrogenated compound comprises $\text{C}_3\text{F}_7\text{H}$.

Replacement sheet 54, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

29. A process for purifying $\text{CF}_3\text{CFHCF}_3$ comprising distilling a mixture comprising $\text{CF}_3\text{CFHCF}_3$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$, and at least one chlorofluorocarbon to form a solution comprising $\text{CF}_3\text{CFHCF}_3$.

30. The process of claim 31 wherein the at least one chlorofluorocarbon comprises C_3ClF_7 .

31. The process of claim 32 wherein the mixture comprises a mole ratio of the chlorofluorocarbon to the $\text{CF}_3\text{CFHCF}_3$ of from about 0.1 to about 10.

32. The process of claim 33 wherein the mixture comprises a mole ratio of the chlorofluorocarbon to the $\text{CF}_3\text{CFHCF}_3$ of at least about 1:2.

33. A process for purifying chlorofluorinated compounds comprising:
providing a reaction product comprising HCl , HF , and a C-3 chlorofluorinated compound;

phase separating the reaction product into a gas phase comprising the HCl , a top liquid phase comprising the HF , and a bottom liquid phase comprising the C-3 chlorofluorinated compound; and

removing the bottom liquid phase to form a solution comprising the C-3 chlorofluorinated compound.

34. The process of claim 35 wherein the C-3 chlorofluorinated compound comprises $\text{C}_3\text{F}_7\text{Cl}$.

35. The process of claim 36 wherein the phase separating comprises altering the reaction product temperature to a temperature of from about 20°C to about 75°C .

36. The process of claim 37 wherein the temperature is about 25°C .

37. A process for purifying reaction products comprising:
providing a reaction product comprising HF and at least one C-3 chlorofluorinated compound;

phase separating the reaction product into a top liquid phase comprising HF and a bottom liquid phase comprising the at least one C-3 chlorofluorinated compound; and

physically separating the top and bottom phases to form a solution comprising the at least one C-3 chlorofluorinated compound.

38. The process of claim 39 wherein the C-3 chlorofluorinated compound comprises a C-3 chlorofluorinated compound having at least six fluorine atoms.

Replacement sheet 55, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

39. The process of claim 40 wherein the phase separating comprises altering the reaction product temperature to a temperature of from about -30°C to about -10°C .
40. The process of claim 41 wherein the temperature is about -20°C .
41. A process for separating chlorofluorinated compounds comprising:
5 providing a first solution comprising both first and second C-3 chlorofluorinated compounds, the first compound having at least six fluorine atoms and the second compound having less than six fluorine atoms;
preparing a mixture comprising the first solution and water;
phase separating the mixture into at least three phases; a gas phase
10 comprising the first compound, an upper liquid phase comprising the water, and a lower liquid phase comprising the second compound; and
removing the gas phase from the upper and lower liquid phases to form a second solution comprising the first compound.
42. The process of claim 43 wherein the mixture further comprises a basic
15 compound.
43. The process of claims 43 or 44 wherein the basic compound comprises KOH.
44. The process of claims 43 or 44 wherein the first compound comprises $\text{C}_3\text{F}_6\text{Cl}_2$ and the second compound comprises $\text{C}_3\text{F}_5\text{Cl}_3$.
- 20 45. The process of claims 43 or 44 wherein the first compound comprises $\text{C}_3\text{F}_6\text{Cl}_2$, and the second compound comprises $\text{C}_3\text{F}_5\text{Cl}_3$ the phase separating comprises altering the first solution reaction temperature to a temperature of from about 25°C to about 75°C .
46. The process of claims 43 or 44 wherein the first compound comprises
25 $\text{C}_3\text{F}_6\text{Cl}_2$ and the second compound comprises $\text{C}_3\text{F}_5\text{Cl}_3$ the phase separating comprises altering the first solution reaction temperature to a temperature of about 50°C .
47. A process for purifying chlorofluorinated compounds comprising:
providing a first mixture comprising both first and second isomers of a C-3
chlorofluorinated compound, the first mixture having a first ratio of the first isomer to the
30 second isomer; and
contacting the mixture with a catalyst to form a second mixture comprising a second ratio of the first isomer to the second isomer, wherein the first ratio is less than the second ratio.

Replacement sheet 56, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

WO 03/029173

PCT/US02/30729

48. The process of claim 49 wherein the contacting further comprises heating the mixture to a temperature of from about 250°C to about 350°C.

49. The process of claim 49 wherein wherein the contacting further comprises heating the mixture to a temperature of about 280°C

5 50. The process of claim 49 further comprising separating at least a portion of the first isomer from the second mixture wherein the separating comprises distilling the second mixture to form a solution comprising the portion of the first isomer.

51. The process of claims 49, 50, 51 or 52 wherein the C-3 chlorofluorinated compound comprises $C_3F_6Cl_2$, the first isomer comprises $CF_3CCl_2CF_3$, and the second
10 isomer comprises $CF_3CClFCF_2Cl$.

52. The process of claims 49, 50, 51 or 52 wherein the C-3 chlorofluorinated compound comprises C_3F_7Cl , the first isomer comprises $CF_3CClFCF_3$, and the second isomer comprises $CF_3CF_2CF_2Cl$.

53. The process of claims 49, 50, 51 or 52 wherein the catalyst comprises
15 chromium.

54. A process for halogenating compounds comprising:
providing a first mixture comprising both first and second isomers of a hydrofluorinated compound, the first mixture having a first ratio of the first isomer to the second isomer; and

20 contacting the mixture with a halogenating agent to form a second mixture having a second ratio of the first isomer to the second isomer, the first ratio being less than the second ratio.

55. The process of claim 56 further comprising separating at least a portion of the first isomer from the second mixture wherein the separating comprises distilling the
25 second mixture to form a solution comprising the portion of the first isomer.

56. The process of claim 56 further comprising contacting the mixture with the halogenating agent in the presence of a catalyst.

57. The process of claims 56, 57 or 58 wherein the hydrofluorinated compound comprises C_3F_7H , the first isomer comprises CF_3CFHCF_3 , and the second isomer
30 comprises $CF_3CF_2CF_2H$.

58. The process of claims 56, 57, or 58 wherein the contacting comprises heating the mixture to a temperature of from about 200°C to about 350°C.

Replacement sheet 57, Under Article 34

Empfangszeit 6.Feb. 0:04

AMENDED SHEET

59. The process of claims 56, 57, or 58 wherein the contacting comprises heating the mixture to a temperature of at least about 300°C.

60. The process of claims 56, 57, or 58 wherein the halogenating agent comprises Cl₂.

5 61. The process of claims 56, 57, or 58 wherein the halogenating agent comprises Cl₂ and a molar ratio of the Cl₂ to the mixture is from about 0.16:1 to about 3:1.

62. The process of claims 56, 57, or 58 wherein the halogenating agent comprises Cl₂ and a molar ratio of the Cl₂ to the mixture is at least about 2.5:1.

63. The process of claims 57 or 58 wherein the catalyst comprises activated
10 carbon.

Replacement sheet 58, Under Article 34

Empfangszeit 6. Feb. 0:01 AMENDED SHEET

TOTAL P. 24

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